

# *The active dissolution of tin in acidic chloride electrolyte solutions - a rotating disc study*

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The anodic dissolution of tin in acidic chloride electrolyte has been investigated using the rotating disc technique. The dissolution reaction has a Tafel slope of  $64 \pm 5$  mV dec<sup>-1</sup> after the effects of diffusion are eliminated. The order of reaction with respect to Cl<sup>-</sup> ion has been found to be unity. The measured currents were also found to depend on C<sub>H<sup>+</sup></sub>. The suggested mechanism involves quasi-reversible charge transfer.

A possible explanation is given for the observed current-time behaviour at low anodic current densities.

## Notation

$i$	Current density
$i_{(\infty)}$	Current density at infinite rotation speed
$i_{d, Cl^-}$	Limiting current density due to Cl <sup>-</sup> diffusion
$C_{Cl^-}$	Concentration of chloride ion
$C_{H^+}$	Concentration of hydrogen ion
$D_0$	Diffusion coefficient of oxidised species
$k_b$	Rate constant for reduction of oxidised species
$\nu$	Kinematic viscosity
$\omega$	Angular velocity
$\alpha$	Anodic transfer coefficient
$k^{\ominus}$	Rate constant at standard equilibrium potential
→	Direction of reaction

## 1. Introduction

The anodic behaviour of tin in chloride media has been little studied, the resultant data often being confusing.

Steinherz [1] detected a critical passivating potential, in the presence of HCl, above which the current density fell abruptly and the dissolution of the metal ceased, the phenomenon being accompanied by a darkening of the electrode. An increase in dilution of chloride ion was found to drive the critical potential to more positive values.

Unfortunately the majority of the experiments were carried out in unstirred electrolyte and when a rotating disc electrode was used the critical potential moved considerably to more positive values.

Hoar [2], however, studied the corrosion of tin in nearly neutral solutions. In order to explain the observed potential-time behaviour he deduced that repair of the pre-immersion film takes place firstly as a result of the anodic formation of oxide within its pores. However when the anodic areas at the base of these pores are sufficiently polarised, due to deficiency of OH<sup>-</sup> ion, a sufficient amount of soluble Sn (II) ions may be produced there to give undermining and film breakdown, concentrated chloride solutions giving more rapid breakdown than dilute. Hoar also showed by the use of potential-pH diagrams representing the equilibrium potentials of the systems Sn/SnO, Sn/SnO<sub>2</sub> and Sn/Sn(OH)Cl (the latter for a 0.1 M KCl concentration) that, under these conditions, the basic salt Sn(OH)Cl is formed in preference to any other oxide when the pH < 2.5.

Straumanis *et al.* [3] found that tin dissolved solely as Sn<sup>2+</sup> ions when dissolved anodically without the use of an external current from tin amalgam in aqueous solutions of HCl. Darkening of the electrode surface occurred as a result of the uneven electrolytic attack.

A more recent investigation by Johnson *et al.*

[4] concerned the anodic dissolution of tin in acidic chloride solutions ( $\text{pH} = -2.0$  to  $2.9$ ). They reported that the apparent valence of the dissolving ions varied from about  $0.4$ – $2.4$  and was a function of both electrolyte and current density. The proposed reaction mechanism involved stepwise oxidation of tin, with  $\text{SnCl}_3^-$  the final reaction product.

The purpose of the present study is to increase the electrochemical knowledge of this system by the use of a rotating disc electrode.

## 2. Experimental

Measurements were made on a tin disc (99.999% pure, diameter 3 mm) with a counter electrode of platinum sheet and the reference a wick type saturated calomel electrode. The solutions investigated were  $0.1$ – $5$  M HCl with additions of KCl. AnalaR grade reagents and triply distilled water from deionised stock were used throughout. All solutions were deoxygenated with nitrogen and at a temperature of  $23 \pm 2^\circ \text{C}$ . A nitrogen atmosphere was maintained above the test solutions at all times. The test electrode was polished on roughened glass prior to introduction to the cell at the required potentials.

The instrumentation has been described previously [5].

## 3. Results and discussion

### 3.1. Normal behaviour

A typical steady state  $E$ – $i$  curve for tin in  $0.1$  M HCl from hydrogen evolution to lattice dissolution is shown in Fig. 1. The electrode was held at  $-950 \text{ mV}^*$  for 1 h before measurements were made to reduce any films on the electrode surface. The current was measured after 1 min at each of the subsequent potentials. This curve is similar to that shown by Golubev *et al.* [6] for tin in  $0.1$  M NaCl.

The currents for active dissolution were a function of rotation speed including those at potentials for which  $i \ll i_{d, \text{Cl}^-}$ . The rotation speed dependence is therefore due to the diffusion of reaction product away from the electrode. For

\* All potentials are quoted with respect to the saturated calomel electrode at the temperature of the experiment.

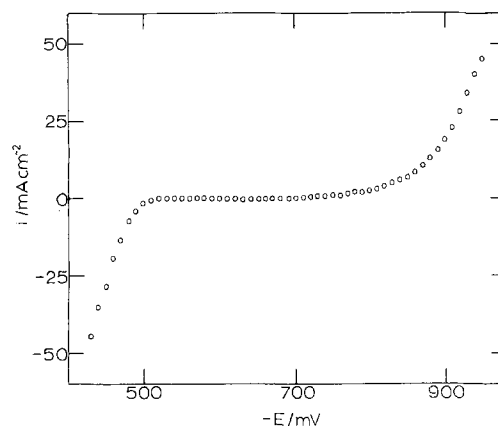


Fig. 1. Typical steady state  $E$ – $i$  curve for tin in  $0.1$  M HCl at a rotating tin electrode.  $\omega = 120 \text{ s}^{-1}$ .

$i \ll i_{d, \text{Cl}^-}$  and assuming the deposition is first order in reaction product:

$$i^{-1} = i_{(\infty)}^{-1} + K\omega^{-1/2}$$

where

$$K = 1.61k_b D_0^{-2/3} \nu^{1/6} i_{(\infty)}^{-1}$$

Typical  $i^{-1}$  versus  $\omega^{-1/2}$  plots at various potentials in  $1$  M HCl are shown in Fig. 2. The variations of slopes of such plots with potential are shown in Figs. 3 and 4 for all solutions investigated. The lines are drawn at  $30 \text{ mV dec}^{-1}$  and are indicative of a reversible two electron change. The reaction is therefore quasi-reversible at the potentials investigated. The potential dependence of  $i_{(\infty)}$  is shown in Figs. 5 and 6. The Tafel slope has a value of  $64 \pm 5 \text{ mV dec}^{-1}$  (lines drawn at  $64 \text{ mV dec}^{-1}$ ). The dependence of  $i_{(\infty)}$  on concentration of both chloride and hydrogen ion is also shown in Figs. 5 and 6. At potentials more positive than those shown, the slope dependence on potential tended towards a value  $> 30 \text{ mV dec}^{-1}$  while the Tafel slope deviated significantly from a value of  $64 \pm 5 \text{ mV dec}^{-1}$ .

Assuming a Tafel slope value of  $64 \text{ mV dec}^{-1}$  the order of reaction with respect to  $\text{Cl}^-$  was calculated at two different hydrogen ion concentrations i.e.  $0.1$  and  $2.5$  M. The order of reaction plot is shown in Fig. 7 with the lines drawn such that

$$\left[ \frac{\partial \log i_{(\infty)}}{\partial \log C_{\text{Cl}^-}} \right]_{E, C_{\text{H}^+}} = 1.0.$$

The order of reaction with respect to  $\text{H}^+$  was also determined and found to be dependent on the chloride concentration, i.e.

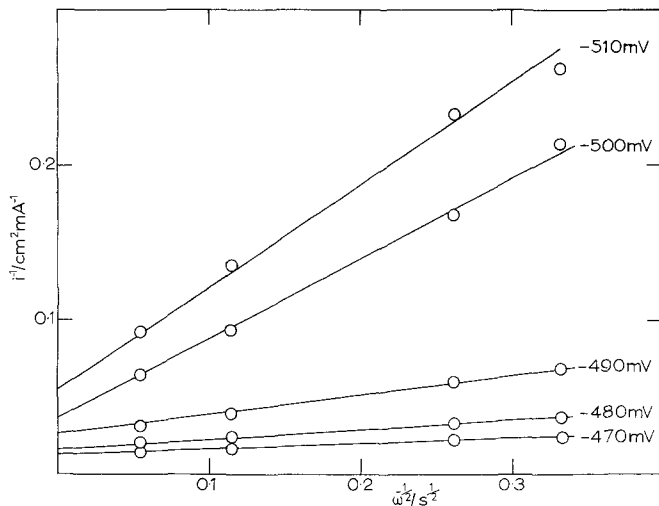


Fig. 2.  $i^{-1}$  versus  $\omega^{-1/2}$  for potentials shown in 1 M HCl.

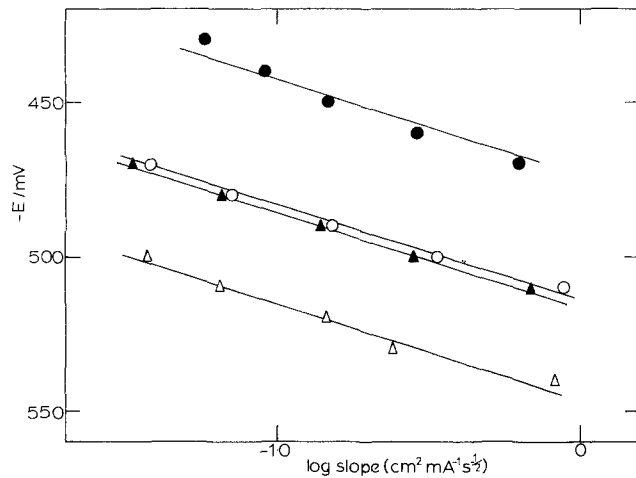


Fig. 3. Variation of slope with potential: 0.1 M  $\text{H}^+$  0.1 M  $\text{Cl}^-$  (●); 0.1 M  $\text{H}^+$  1.0 M  $\text{Cl}^-$  (○); 1.0 M  $\text{H}^+$  1.0 M  $\text{Cl}^-$  (▲); 0.1 M  $\text{H}^+$  2.5 M  $\text{Cl}^-$  (△).

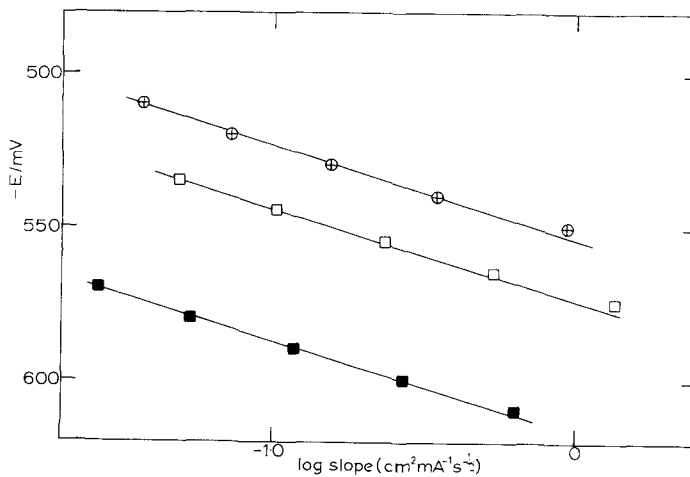


Fig. 4. Variation of slope with potential: 2.5 M  $\text{H}^+$  2.5 M  $\text{Cl}^-$  (⊕); 2.5 M  $\text{H}^+$  5.0 M  $\text{Cl}^-$  (□), 5.0 M  $\text{H}^+$  5.0 M  $\text{Cl}^-$  (⊞).

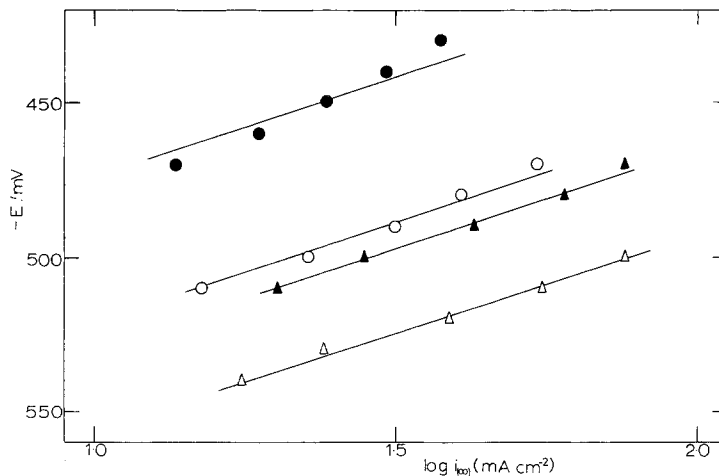


Fig. 5. Tafel plots for tin dissolution: 0.1 M H<sup>+</sup> 0.1 M Cl<sup>-</sup> (●), 0.1 M H<sup>+</sup> 1.0 M Cl<sup>-</sup> (○), 1.0 M H<sup>+</sup> 1.0 M Cl<sup>-</sup> (▲), 0.1 M H<sup>+</sup> 2.5 M Cl<sup>-</sup> (△).

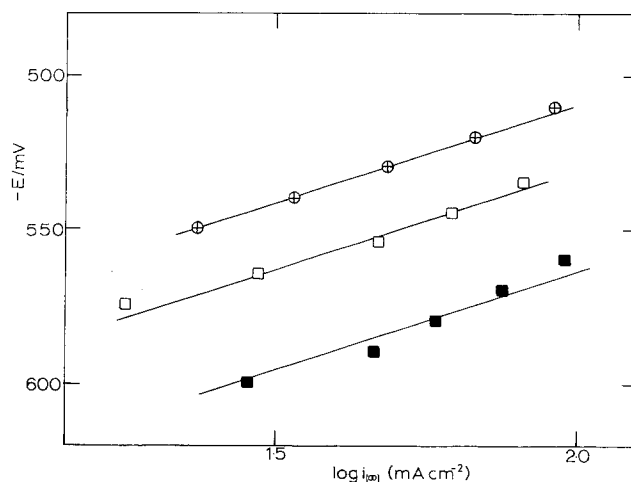


Fig. 6. Tafel plots for tin dissolution: 2.5 M H<sup>+</sup> 2.5 M Cl<sup>-</sup> (⊕), 2.5 M H<sup>+</sup> 5.0 M Cl<sup>-</sup> (□), 5.0 M H<sup>+</sup> 5.0 M Cl<sup>-</sup> (■).

$$\left[ \frac{\partial \log i_{(\infty)}}{\partial \log C_{H^+}} \right]_{E, C_{Cl^-}=1} = 0.14$$

$$\left[ \frac{\partial \log i_{(\infty)}}{\partial \log C_{H^+}} \right]_{E, C_{Cl^-}=2.5} = 0.18$$

$$\left[ \frac{\partial \log i_{(\infty)}}{\partial \log C_{H^+}} \right]_{E, C_{Cl^-}=5.0} = 1.7.$$

In addition to the rotating disc experiments a number of impedance measurements were made at a stationary upward facing electrode in the frequency range 10 K – 4 Hz using a Schering bridge incorporating a phase sensitive detection system.

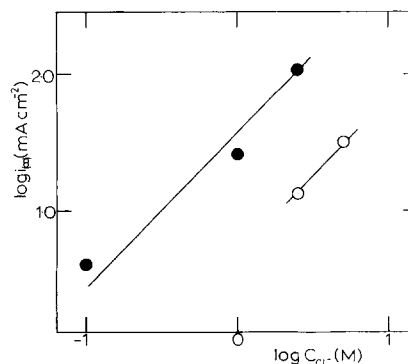


Fig. 7. Order of reaction plot for Cl<sup>-</sup> ion (●) C<sub>H<sup>+</sup></sub> = 0.1 M, E = -490 mV. (○) C<sub>H<sup>+</sup></sub> = 2.5 M, E = -560 mV.

A typical complex plane plot is shown in Fig. 8 for 0.1 M HCl at  $-525$  mV. The form of the plot confirms that the reaction is controlled by both charge and mass transfer, showing a semi-circle at high frequencies and a  $45^\circ$  straight line at lower frequencies. The distortion of the semi-circle may be the result of surface roughness since it is known that an infinitely rough electrode would give a quarter-circle in a complex plane display. The current-time behaviour at potentials close to  $-525$  mV (discussed in a later section) indicates that filming of the electrode may be taking place during the time of the experiment; this may also contribute to the observed distortion.

Johnson *et al.* [4] have measured anodic Tafel slopes of value  $\sim 30$  mV  $\text{dec}^{-1}$  from steady state  $E-i$  curves. They concluded from this value together with the observed superimposition of such  $E-i$  curves at approximately constant  $C_{\text{Cl}^-}$  but different pH (1.2–2.9) that the reaction sequence involved two equilibrium charge transfer reactions and a following chemical rate-determining step with neither  $\text{H}^+$ ,  $\text{OH}^-$  nor  $\text{H}_2\text{O}$  being involved in either of the two processes. This argument, however, requires revision in the light of a knowledge of the true kinetic currents. A further argument [4] involving a measured value of  $\partial E/\partial \log a_{\text{Cl}^-}$  at constant current density for the determination of an order of reaction (w.r.t.  $\text{Cl}^-$ ) also requires some extension by the inclusion of  $\alpha$  the charge transfer coefficient. A further examination of previously reported voltammograms [4] for the anodic dissolution of tin in acidic chloride solution show them to be  $iR$  controlled; in fact a linear relation-

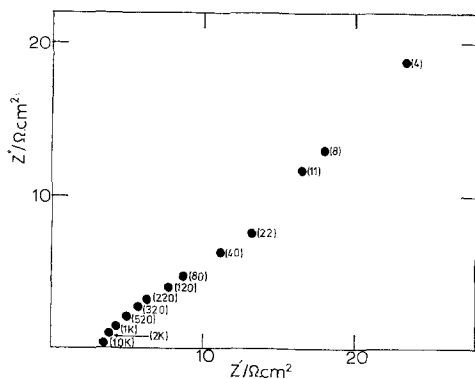
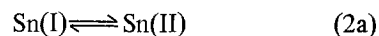


Fig. 8. Typical complex plane plot for tin in 0.1 M HCl ( $E = -525$  mV) at a stationary upward facing electrode.

ship was recognised between current and potential over the current density range 20–80  $\text{mA cm}^{-2}$ .

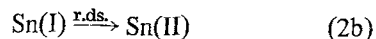
If we consider the possibility of a stepwise reaction with a single limiting step there are two possibilities:



from which:

$$\frac{\partial E}{\partial \log i} = \frac{0.059}{\alpha}$$

Putting  $\alpha = 0.5$  gives an expected Tafel slope value of  $\sim 120$  mV  $\text{dec}^{-1}$ . For a Tafel slope of value 64 mV  $\text{dec}^{-1}$ ,  $\alpha$  needs to be  $\sim 0.92$ . This is unlikely.

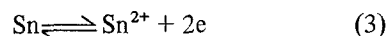


from which:

$$\frac{\partial E}{\partial \log i} = \frac{0.059}{(1 + \alpha)}$$

Putting  $\alpha = 0.5$  gives a Tafel slope value of  $\sim 40$  mV  $\text{dec}^{-1}$ . A value of  $\sim 0.08$  for  $\alpha$  is required to give a Tafel slope value of 64 mV  $\text{dec}^{-1}$ . This is again unlikely.

If there is simultaneous transfer of two electrons, i.e.



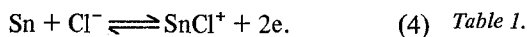
then

$$\frac{\partial E}{\partial \log i} = \frac{0.059}{2\alpha}$$

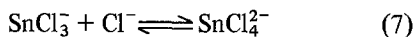
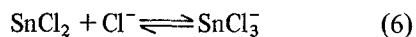
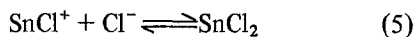
Using  $\alpha = 0.5$  gives a Tafel slope value of  $\sim 60$  mV  $\text{dec}^{-1}$  while the experimentally observed Tafel slope value of 64 mV  $\text{dec}^{-1}$  can be realized with  $\alpha = 0.46$ .

It would appear therefore that the most appropriate reaction mechanism involves simultaneous two electron transfer. This conclusion is of interest in view of the work of Gorodetskii [10] with dilute Sn amalgams in perchloric acid solutions where breaks in Tafel curves indicated single electron steps. It is likely that with a divalent metal the first step is very fast (e.g. Cu, Zn etc.) and is followed by a rate-determining electron transfer step. It seems probable in the case of tin in chloride solutions that the second electron transfer is also fast, making it impossible to resolve the overall transfer into its components with the present methods.

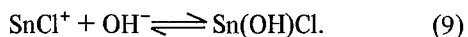
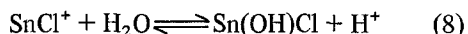
Taken with an order of reaction with respect to  $\text{Cl}^-$  of unity, the charge transfer mechanism in chloride solution is most probably:



The  $\text{SnCl}^+$  ion then undergoes a number of chemical reactions in solution, i.e.



together with



The effect of  $\text{H}^+$  can be related to Reactions 8 and 9. At lower pH values formation of the sparingly soluble oxy-chloride, whose precipitation on or close to the electrode surface would result in blocking of the electrode, is inhibited. At higher  $C_{\text{H}^+}$  the order of reaction with respect to  $\text{H}^+$  appears to increase markedly. No satisfactory reason could be found for this, however, and it may be due to a number of factors. Firstly the inclusion of such a high  $C_{\text{H}^+}$  may constitute a solvent change. Secondly in our experiments it was difficult to eliminate junction potentials in the higher  $C_{\text{H}^+}$  range. The possibility of the formation of various complexes is increased. All these factors would tend to increase the exchange current, particularly the first and last where the  $\text{Sn(II)}$  ion may receive considerable stabilization in the higher acid environment.

The standard equilibrium potential for the  $\text{Sn/Sn}^{2+}$  system was used to calculate  $k^\ominus$  in 1 M HCl and its value was found to be  $1.6 \times 10^{-5} \text{ cm s}^{-1}$ .

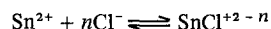
The identity of the final solution species is uncertain. Data for the equilibrium constants of Reactions 5–7 are given in Table 1. From these it would be expected that  $\text{SnCl}_2$  would be the most abundant solution species, while there is some doubt [7] about the presence of the highly charged  $\text{SnCl}_4^{2-}$  species.

### 3.2. Current-time behaviour at low current densities

Fig. 9 shows the current-time behaviour of tin in 0.1 M HCl at a potential of  $-540 \text{ mV}$ . The current which is initially anodic decreases with time, eventually becoming cathodic and of fairly con-

Reaction	$K^\ddagger$	[8]	[9]
(5)	3.6	5.1	5.5
(6)	0.96	0.24	0.6
(7)	$\leq 0.2$	1.0	0.3

† Calculated by the authors from the equilibrium constants determined by Vanderzee *et al.* [7] for the following reaction:



where  $n = 0, 1, 2, 3, 4$ .

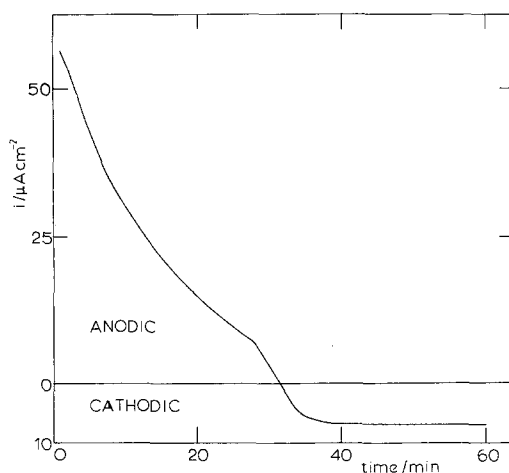


Fig. 9. Current-time curve for a rotating tin electrode in 0.1 M HCl.  $\omega = 120 \text{ s}^{-1}$ ,  $E = -540 \text{ mV}$ .

stant value. During this time the electrode capacitance at 10 kHz decreased from  $\sim 40 \mu\text{F cm}^{-2}$  to  $\sim 10 \mu\text{F cm}^{-2}$  and was accompanied by an increase in resistance. This behaviour may indicate the formation of a film that is thickening and/or tightening with time. Hoar [2] has shown that at a  $\text{pH} < 2.5$  any film formed, in the absence of current, is most likely to consist of  $\text{Sn(OH)Cl}$ . It may be, therefore, that the filming reaction is also present when an anodic current is flowing causing passivation and dissolution through a film.

Fig. 10 shows the effect on this behaviour of moving to more positive potentials. At  $-510 \text{ mV}$  the behaviour is initially similar to that exhibited at  $-540 \text{ mV}$  in that the current falls with time. However, at longer times the current reaches a minimum value after which it begins to increase. This increase of current with time is probably the result of a breakdown of the initially formed film

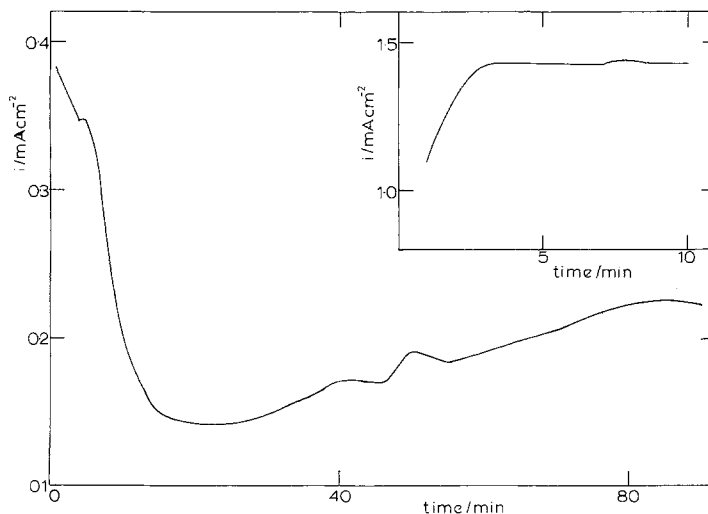


Fig. 10. Current-time curve for rotating tin electrode in 0.1 M HCl.  $\omega = 120 \text{ s}^{-1}$ ,  $E = -510 \text{ mV}$ . Inserted current-time curve at  $-500 \text{ mV}$ .

resulting in an increased rate of dissolution possibly accompanied by area increases. This explanation is essentially the same as that given by Hoar [2] for the time dependence of the rest potentials of tin in neutral solutions. Moving to  $-500 \text{ mV}$  produces a significant change in the resultant time behaviour (Fig. 10). At this potential the current rises initially before becoming fairly time independent. This change may be related to a shift in emphasis from  $\text{Sn-OH}^-$  inter-

actions to  $\text{Sn-Cl}^-$  interactions at the electrode surface. This change may significantly reduce the amount of  $\text{Sn(OH)Cl}$  produced and hence prevent blockage of the electrode surface.

The effect of an increase in  $C_{\text{Cl}^-}$  is shown in Fig. 11. Comparison between Fig. 11 and that behaviour shown in Fig. 9 indicates that following film formation (current falls with time) the increase in  $C_{\text{Cl}^-}$  causes the film breakdown to occur and an increased rate of dissolution (current in-

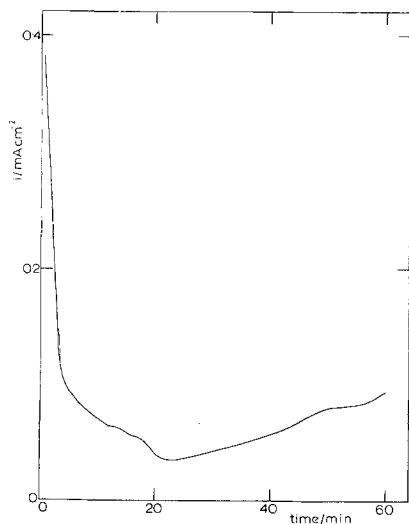


Fig. 11. Current-time curve for a rotating tin electrode in a solution containing 0.1 M  $\text{H}^+$  and 0.9 M  $\text{Cl}^-$ .  $\omega = 120 \text{ s}^{-1}$  and  $E = -540 \text{ mV}$ .

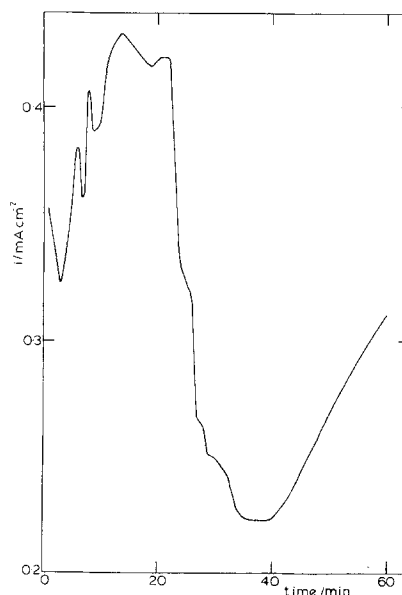


Fig. 12. Current-time behaviour for a rotating tin electrode in 1.0 M HCl.  $\omega = 120 \text{ s}^{-1}$  and  $E = -540 \text{ mV}$ .

creases with time). Again this would be the result of an increase in Sn-Cl<sup>-</sup> interactions.

Fig. 12 shows the effect of a decrease in pH. The resultant current-time curve is more complicated than that shown at higher pH. However, it is essentially the same as that shown in Fig. 11 with the breakdown point (minimum in curve) at a shorter time. Hydrogen ion facilitates breakdown, probably by reducing the time required for a sufficient decrease in OH<sup>-</sup> ions at the surface to produce Sn(II) ions and hence breakdown.

The enhanced h.e.r. at this pH may have affected the observed currents, although this may be considered unlikely in view of the high hydrogen overvoltage of tin.

#### Acknowledgement

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